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PROCESSING OF OIL SHALE IN MOLTEN HYDROXIDES

By

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INTRODUCTION

Current processes for the production of organics from oil shale are all variations of high-temperature pyrolysis. All such processes are subject to similar problems: handling solids is more difficult than handling liquids; much of the carbon is unrecoverable owing to the nature of organic pyrolysis; and the product is primarily a synthetic petroleum that must be further refined before it can be used as a fuel. The use of a molten-salt medium at lower temperatures may ameliorate these problem areas.

An earlier survey study to identify suitable salts for solvents gave no promising candidate systems (1). Processing in a tetrachloroaluminate melt at 320°C gave a variety of products soluble in organic solvents (2), but this temperature is still relatively high and carbon conversion was apparently limited by hydrogen disproportionation. Aqueous alkali has been shown to decompose coal to lower molecular weight products at somewhat lower temperatures (3).

The preliminary studies herein described have identified a candidate molten salt, a mixture of lithium, sodium and potassium hydroxides and some of its processing characteristics have been identified. Preliminary results on the effects of temperature, time and presence of oxygen show that processing at 200-225°C in the presence of oxygen and water gives an organic product consisting of a hydrocarbon fraction in the gasoline-diesel fuel range and an acid fraction that may be useful for plastics or resin manufacture. Very little further refining appears to be necessary for these products. A potential problem is the dissolution of silica and other mineral matter in the molten salt.

METHOD

A combustion furnace was set up to allow the shale to be heated in a controlled atmosphere (Figure 1). A glass liner for the furnace was fitted to a flowmeter and tanks of the gases to be used. A glass U-tube was used to collect the product fraction condensable in a dry-ice-methanol slush. Gases were not collected, but they appear to have been a minor product. Noncondensable gases would have been CO, CO₂, methane, ethylene and acetylene. Shale and hydroxide mix (1 NaOH: 1 KOH: 0.5 LiOH) were measured into a nickel liner in a stainless steel boat and inserted into the furnace for various times, which were measured from the insertion of the boat to its removal. Duplicates were performed for most runs. The melting point of the hydroxide mix alone was 147-151°C.

All of the solids to be processed were ground into relatively small particles. In particular, the oil shale was ground in a ball mill and sieved to give fractions of less than 495 microns particle diameter. Grinding was necessary only for reproducibility, however. Chunks of shale up to a few centimeters diameter were easily dissolved in liquid hydroxide.

This apparatus has some heat and mass transfer limitations. Some dependence of apparent reaction rate on sample size was observed, with 200- and 500-mg samples of shale giving different results than 1-g samples when processed with hydroxide in a 1:5 shale:hydroxide ratio. A 2-g sample gave a similar result to the 1-g sample. This same effect was observed in pyrolysis of shale without hydroxide. In addition, condensate collected from the hydroxide mixture heated alone at 200°C for 30 min was independent of hydroxide mass, giving essentially the same amount of condensate for 1, 2.5, 5 and 10 g of hydroxide. The rate of absorbed water loss by the hydroxide mixture under these conditions is evidently more of a function of the surface area of the melt than of the quantity of hydroxide present.

A 1-g portion of shale was heated with 10 g of hydroxide for 30 min, to determine the effect of a change in the shale-to-hydroxide ratio. No change was observed from the results for the 1:5 ratio.

Products were contained both in the condensate and in the shale-hydroxide melt, which

upon cooling formed a brick. Separation of the solid products consisted of

1. dissolving the brick in distilled water,
2. filtration of solids,
3. extraction of the filtrate with diethyl ether,
4. acidification of the aqueous fraction with HCl,
5. removal of precipitates by filtration,
6. extraction of acidified filtrate with ether.

The filtrate was then evaporated, as were the ether extracts, and the residues retained.

The organic products were recovered mainly in the ether extracts, but the evaporated salt from the acidified filtrate also appeared to contain acids. This method must be considered semi-quantitative, as not all the variables are well known. For example, one of the precipitates that forms upon acidification is apparently a carbonate; at some low pH, it decomposes to CO₂ gas and soluble species. The decomposition point seems to vary from one set of processing conditions to another. Thus, comparable quantities and compositions of these precipitates could not be obtained.

Analysis of the separated organic components was by NMR and GC-MS. Spot tests (4) were attempted for sulfur and other inorganic components in the aqueous solution from the processed brick, but results were not interpretable, probably because of the presence of organic complexants.

RESULTS AND DISCUSSION

Effect of Process on Different Materials

Several types of oil shale and other materials were processed with the 1 NaOH: 1 KOH: 0.5 LiOH mix at 200°C. The oil shales were Green River, Cleveland (Kentucky), Gassaway, Huron and Dowelltown. Fruitland subbituminous coal, wood sawdust and Santa Rosa tar sand were also treated. Samples of each of these materials were also heated without hydroxide. Processing with hydroxide doubled the condensate yield from the coal and tripled the yield from the sawdust. In addition, the sawdust was converted almost completely to water-soluble products. The effect of the hydroxide on the tar sand appeared to be negligible; both in hydroxide yield and in organics contained in the melt.

The shales all gave markedly increased yields of condensate when processed with hydroxide at 200°C for 60 min. The amounts of condensate from shale only and the shale-hydroxide mix are given in Table I. Only qualitative observations have been made of the products contained in the melt. Filtrates from Green River and Cleveland shales are a light yellow. The filtrates from the other Eastern shales are much darker, suggesting increased amounts of aromatic acids, particularly phenols and possibly some complexing of metals liberated from the inorganic fraction. The filtrates from all of the shales but Dowelltown and Green River have strong, petroleum-like odors, while the shales before processing have little odor.

TABLE I

CONDENSIBLES FROM OIL SHALE PROCESSING (mg/g Shale)

<u>Shale Type</u>	<u>Shale Alone</u>	<u>Shale and Hydroxide</u>
Green River	22.0	94.2
Cleveland	18.7	101.3
	16.7	103.6
Gassaway	14.2	101.2
Huron	17.8	114.2
Dowelltown	15.7	103.0

Upon acidification, the filtrates give off a gas that has an H₂S odor and blackens lead acetate paper. This suggests that the sulfur in the shales is being retained in the melt in a water-soluble form. Standard spot tests (4) for sulfur in the filtrates were inconclusive, however.

GC-MS analysis of the condensate from Green River shale shows hydrocarbons with molecular weights up to about 200. These include relatively unbranched alkanes and alkenes, cycloalkanes and possibly aromatics. Proton and ¹³C NMR of the ether extract from the basic solution shows a similar group of compounds, presumably of higher molecular weight, since they were not distilled from the melt. The NMR spectrum is clean enough to suggest that the molecular weights are probably not extremely high, or that the molecular structure is relatively regular. NMR analysis of the ether extract from the acid solution shows acids, some of which may have complex structures involving bridged rings. No other heteroatom-containing functional groups were observed.

The coal filtrate precipitated a black organic solid upon acidification. This solid gave a proton NMR spectrum with a broad absorption in the aromatic region, suggesting that the compounds are highly aromatic and of high molecular weight, similar to humic acids.

Although both GC-MS and NMR are fairly reliable, stand-alone methods of analysis, these identifications must be regarded as preliminary until they are confirmed by at least one other method, such as IR spectroscopy.

Processing Conditions

To ascertain the ranges of atmospheric composition and processing temperature, Green River shale was used. Samples consisting of 1 g shale and 5 g hydroxide mix, shale only and hydroxide only were heated to temperatures of 200, 225 and 250°C in an atmosphere of 95% Ar and 5% O₂ at a flow of 500 cm³/min for times up to 2 h. The results plotted in Figure 2 represent the net amount of condensate obtained from the shale after correcting for the condensate from a hydroxide blank. An increase in temperature from 200 to 225°C resulted in an increase in the reaction products from the shale-hydroxide mixture, although the temperature effect is small after 2 hours. At 250°C, condensate weights from the shale-hydroxide mixture were erratic because of foaming and swelling of the samples during heating. The pyrolysis rate of the shale alone also increases with heating, but not as rapidly.

Because of the heat and mass transfer properties of the apparatus, these data must be taken as indicative of trends, rather than absolute. The error is not well known, but it seems likely to be +10%.

Yields of the hydrocarbons and acids extracted from the melt also increased with time. However, the yields of the acids appear to be higher for processing at 200°C than at 225°C. Dissolved mineral matter, in the form of the inorganic precipitates that form upon acidification, is much higher for processing at 225°C than at 200°C. These results are semi-quantitative only.

Heating of a 1:5 shale:hydroxide sample in Ar alone yielded only 63% of the amount of condensate obtained when the atmosphere contained 5% O₂. An unusually dry batch of hydroxide mix has much less effect on the reaction of the shale than a wetter batch. Portions of the dry hydroxide were exposed to the laboratory atmosphere for times of one and two hours to absorb moisture, after which they were used in processing Green River shale. Although the blank values varied with exposure time, the condensate yields from the shale processed with the wetter hydroxide agreed well with previous values. The reaction, therefore, appears to involve an oxidative attack on the kerogen structure, with water required for the reaction.

Yields of hydrocarbon in the condensate could not be directly measured. The condensate contains significant amounts of water, which cannot be estimated because of uncertainties in the amounts of water liberated from the oil shale minerals and from the hydroxide by additional bubbling caused by decomposition of the kerogen into gaseous products. However, a minimum value for the yield of organic products can be estimated from the amounts of organics extracted from the melt. A typical value for hydrocarbons extracted from the melt is 15 mg/g shale and for acids, 10 mg/g shale. The total converts to 8 gallons/ton shale, for an assumed density of the organics of 0.72. The shale used in these experiments has a Fischer Assay of 25 gallons/ton shale. The real yield, including the condensable hydrocarbons and the acids left in the filtrate, must be larger than 8 gallons/ton and is made up of compounds having a relatively high H:C ratio in the case of Green River shale.

CONCLUSIONS

Green River oil shale can be processed in a molten NaOH-KOH-LiOH mix in the presence of oxygen and water at temperatures near 200°C to given hydrocarbon and acid products. There appears to be no reason that the process should not work for Eastern oil shales, coal, wood waste and other materials, although it is ineffective for tar sands. A mechanism consistent with the observations would be oxidative attack on kerogen to form carboxylic acid salts, followed by decarboxylation of the salts to hydrocarbons. However, more work is necessary to prove this mechanism. Dissolution of mineral matter appears to be strongly temperature dependent. Nitrogen and sulfur appear to be absent from the products.

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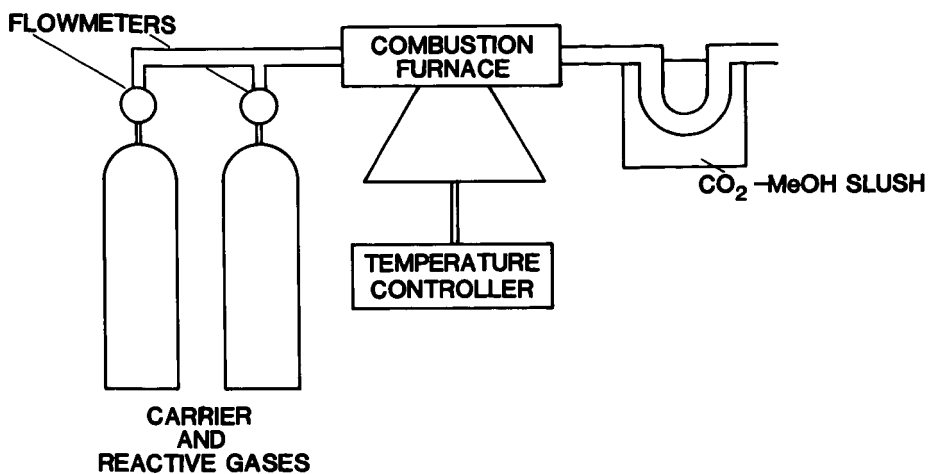


Figure 1. Experimental Apparatus

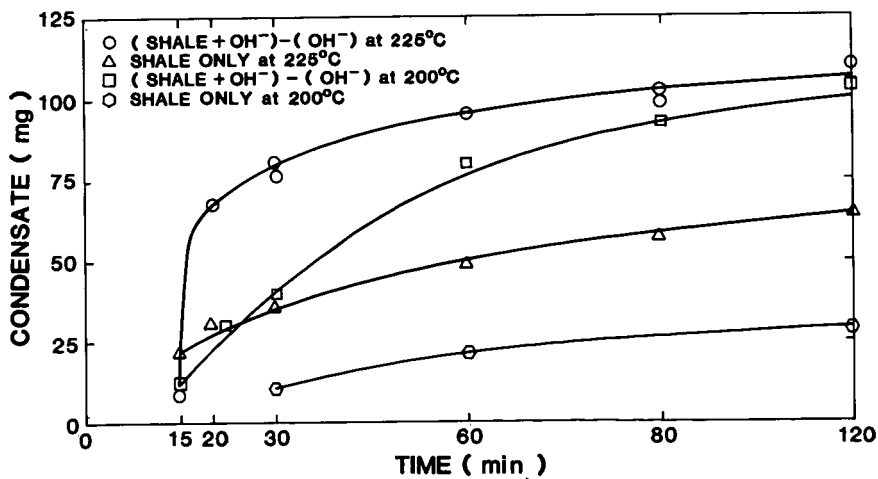


Figure 2. Dependence of condensate product on temperature and time.

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